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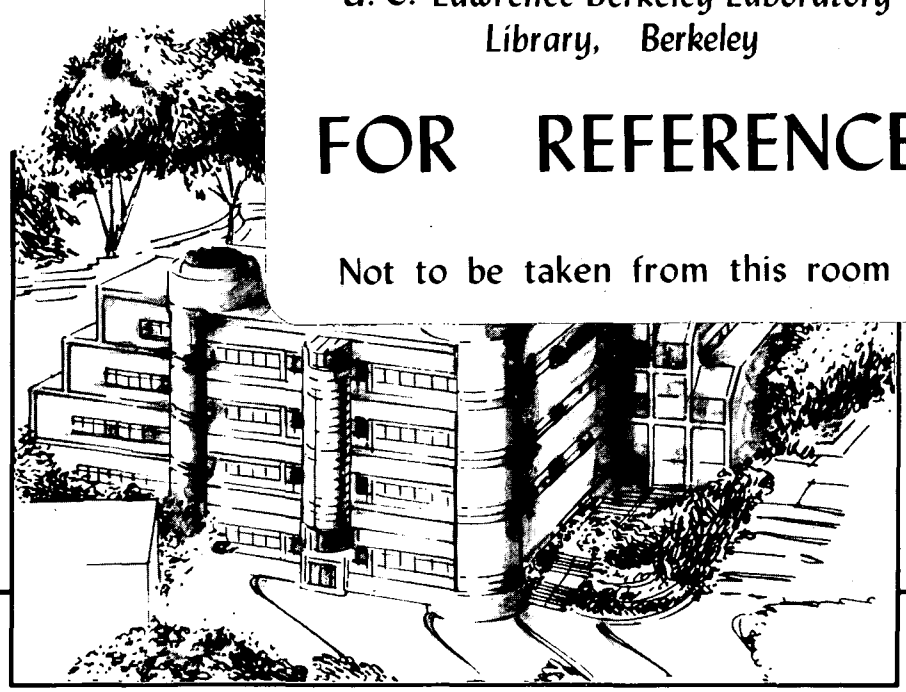

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Scanning tunneling microscopy of Si donors in GaAs

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Keywords: STM, surface state, hydrogenic impurity, GaAs

Abstract

Using scanning tunneling microscopy, we have identified and characterized Si donors (Si_{Ga}) in GaAs located on the (110) surface and in subsurface layers. Si_{Ga} on the surface shows localized features with characteristic structures in good agreement with a recent theoretical calculation [Wang *et al.*, Phys. Rev. B, ***47***, 10329 (1993)]. Si_{Ga} in subsurface layers appears as delocalized protrusions superimposed on the background lattice, which are interpreted in terms of the modification of the tunneling due to the tip-induced band bending perturbed by the Si_{Ga} Coulomb potential.

I. Introduction

The power of scanning tunneling microscopy (STM) for the study of geometric and electronic structure of semiconductor surfaces has long been realized [1, 2]. Recently, the use of STM to investigate the bulk defect properties of semiconductors has been beautifully demonstrated by the study of antisite defects in low-temperature-grown GaAs [3]. The properties of an imperfection in

a bulk semiconductor are often distinctly different from those on a surface, and STM studies of these imperfections will definitely become more important in the future, although up to the present, few such studies have been reported.

Shallow substitutional impurities, such as Si donors (Si_{Ga}) in GaAs, are probably among the best known and best understood imperfections in semiconductors. In the bulk, the electronic structures of these impurities are known to be delocalized and well described by the hydrogenic model. At the surface, broken bonds of these impurities may introduce strongly localized electronic structures and deep states near the middle of the energy gap. In a recent theoretical study, Wang *et al.* [4] predicted that STM images of Si_{Ga} on a GaAs (110) surface should reveal unique, localized electronic structures in voltage-dependent images and current-voltage (I-V) spectra. Experimentally, these localized Si_{Ga} features have never been reported, although Feenstra *et al.* observed fluctuations due to Si on GaAs (110) surfaces in a STM study of doping superlattices [5].

In this work, we performed STM studies on (110) studies of Si-doped GaAs crystals. Localized electronic features were clearly observed. The filled- and empty-state STM images show characteristic electronic structures in good agreement with the theoretical predictions of the Si_{Ga} on the GaAs (110) surface. In addition to these localized structures, Si-related protrusions superimposed on the background atomic lattice were also observed, and we interpret these protrusions in terms of the modification of the tunneling due to the tip-induced band bending perturbed by the Si_{Ga} Coulomb potential.

II. Experiments

Si doped GaAs crystals grown by liquid encapsulated Czochraski technique were studied. Samples from different sources, and with high and low

Si doping concentrations, n^+-GaAs ($2 \times 10^{18}/cm^3$) and n^-GaAs ($5 \times 10^{16}/cm^3$), were investigated. The STM head was similar to that developed by J. Frohn *et al.* [6], which allows the tip to move over a large area of the sample surface. The electronic control was a commercial unit made by RHK [7]. The samples were cleaved in-situ in a ultra-high-vacuum chamber with a base pressure of 8×10^{-11} torr. Electrochemically etched Pt-Rh tips were used. All STM images were obtained in constant current mode with a tunneling current of 0.5 nA.

III. Results and discussion

Localized features observed on the Si-doped GaAs (110) surface (Fig. 1) are attributed to Si_{Ga} donor atoms situated on the cleavage plane based on the theoretical work of Wang *et al.* [4]. The most characteristic images are obtained for sample voltages of -2.5 V (Fig. 1a) and +2.5 V (Fig. 1b), corresponding to filled- and empty-state images, and matching very well with the theoretically predicted images of a Si_{Ga} on GaAs (110) surface at voltages of -1.2 V and +1.9 V, respectively. The theoretical calculation did not consider tip-induced band bending, and assumed a Fermi level at midgap. By taking the band bending into account, and considering that in our sample the Fermi level is at the conduction band edge, the experimental images at -2.5 and +2.5 V should closely correspond to the theoretical images at -1.2 and +1.9 V, respectively. We believe this is the first direct observation of surface Si_{Ga}.

The localized features in Fig. 1 are readily understood if modifications to the electronic structures of the GaAs (110) surface are considered. According to Wang *et al.* [4], when a Si_{Ga} donor atom is on the surface, a state near midgap is introduced due to the dangling bonds of the atom. Since the dangling-bond state has a lower energy than the hydrogenic state of the Si_{Ga} donor in bulk GaAs, the extra electron of the Si_{Ga} is thus trapped in this localized, lower energy state. In

addition, this midgap state interacts with the surface dangling-bond states of neighboring As and Ga. The resulting consequences are: (a) the dangling-bond state of the Si_{Ga} will have an energy slightly above midgap; (b) the dangling-bond states of As atoms adjacent to the Si_{Ga} are pushed to lower energies than their normal positions near the valence bond edge; and (c) the dangling-bond states of Ga atoms adjacent to the Si_{Ga} are also slightly pushed to higher energies than their normal positions near the conduction band edge. The above effects are expected to be localized in the neighborhood of the Si_{Ga}, since the dangling-bond state of the Si_{Ga} is localized to within a few bond lengths.

For a sample voltage of -2.5 V, as seen in Fig. 1a, the tunneling condition has been optimized for electrons to tunnel out of the filled, normal dangling-bond states of As atoms not in the neighborhood of the Si_{Ga}. At this tunneling condition, electrons can also tunnel out of the half-filled, dangling-bond state of the Si_{Ga}. A local maximum is thus observed at the position of the Si_{Ga}. Since the filled, dangling-bond states of the As atoms immediately adjacent to the Si_{Ga} lie at lower energies, the voltage of -2.5 V is not sufficient for electrons to tunnel out of these states. A denuded zone of apparently missing As atoms are therefore observed at the positions of the two As atoms bonded to the Si_{Ga}. Note in Fig. 1a that the two As atoms neighboring the apparently missing As atoms, however, appear brighter, which was not predicted in the theoretical work. At a sample voltage of +2.5 V (Fig. 1b), the image of the surface Si_{Ga} appears significantly different. Electrons tunnel at this voltage from the tip into the dangling-bond states of the Ga atoms. The Ga sublattice on GaAs (110) surface is clearly observed. However, the tunneling into the dangling-bond state of the Si atom is weaker, since the state is half filled. The Si_{Ga} thus appears dark in the image and resembles a missing Ga atom. The Ga atoms neighboring the Si atom also appear dark in the image, since the dangling-bond states of these Ga atoms lie at higher

energies due to the interaction with the Si_{Ga} dangling-bond state, and it is more difficult for electrons to tunnel into these states.

An interesting observation for the localized surface Si_{Ga} feature is that their experimentally measured density is lower than what one would expect from the Si doping concentration of the sample. For instance, for Si doping concentration of $2 \times 10^{18}/cm^3$, the expected density of the Si_{Ga} on a (110) plane would be $4 \times 10^{10}/cm^2$. The reason for the much fewer Si_{Ga} features observed is not fully clear yet. It is, however, suspected to be due to the instability of the Si_{Ga} having half-filled dangling bonds on a cleavage plane. The Si_{Ga} may have left the crystal during cleavage.

In addition to the localized electronic features associated with the Si_{Ga} on the (110) surface, delocalized features (Fig. 2) are also observed. They appear as protrusions superimposed on the background atomic lattice for both the positive and negative sample voltages. These features are believed to be due to subsurface Si since their concentration scales well with the Si doping concentration. Images in Fig. 2 show that the apparent height of the protrusions is strongly bias dependent, and in most cases decreases from ~1 Å at -1.5 V to ~0.1 Å at -3.0 V. The spatial extension of the protrusions decreases slowly with increasing negative sample voltages. The decrease of the extension of the protrusions at increasing positive voltages, however, is less significant. Typically, the spatial extension of the protrusions is ~50 Å (~25 Å at full width half maximum) at -1.5 V, and decreases to about half that value at -3.0 V. We believe these delocalized protrusions are due to Si_{Ga} in bulk GaAs located in subsurface layers below the (110) cleavage plane. In fact, the apparent height of the protrusions measured at the same sample voltage is statistically found to have several discrete values, and are attributed to Si_{Ga} atoms situated in subsurface layers with different distances to the cleavage plane [8].

The delocalized protrusions of a Si_{Ga} in a subsurface layer observed for both positive and negative sample voltages are interpreted in Fig. 3 in terms of the modification of the tunneling due to the tip-induced band bending perturbed by the Si_{Ga} Coulomb potential [9,10]. At positive sample voltages (Fig. 3a), electrons tunnel from the metal tip to the empty conduction band states in the semiconductor. In such conditions, the GaAs subsurface region is expected to be in depletion in analogy to metal-insulator-semiconductor contacts. The Si_{Ga} in the depletion region is positively charged. The Coulomb potentials of the Si_{Ga} (~1/r), with their overlapping tails, give rise to the average band bending in the semiconductor. Close to the core of each of the Si_{Ga}, the Coulomb potential is stronger, which locally decreases the band bending and significantly increases the available states for tunneling. The observed radius of the protrusions (~25 Å) is consistent with the extension of the dominant part of the Coulomb potential (defined as the region where the potential is stronger than kT ~26 meV). At negative sample voltages (Fig. 3b), electrons tunnel from the valence-band states and filled conduction-band states of the semiconductor to the metal tip. In such conditions, the GaAs subsurface region can be brought into accumulation, and the Si_{Ga} is expected to be neutral. However, the potential near the core of the Si_{Ga} is nevertheless significant and approximately proportional to $(1/r)\cdot e^{-2r/a_o}$, where a_o ~ 85 Å is the Bohr radius of the hydrogenic donors in GaAs. Close to the core of the Si_{Ga}, the potential still locally decreases the band energy, resulting in stronger tunneling and hence the observed protrusions. Obviously, the dominant part of the potential (at $r \leq 25$ Å $< a_o/2$) is only slightly different from that of the 1/r potential in depletion. Hence the radius of the protrusions is expected to be ~25 Å, which is consistent with the experimental observations at sample voltage of -1.5 V.

The decrease of the apparent height of the protrusions is expected at both

higher positive and negative sample voltages, since the tunneling is then dominated by a large number of band states available, and is less sensitive to the presence of the Si_{Ga}. The slow decrease of the extension of the protrusions with increasing negative sample voltages may be attributed to the screening of the Si_{Ga} potential by conduction electrons accumulated close to the surface. In bulk GaAs, the calculated characteristic screening length is ~55 Å for an electron concentration of $10^{18}/cm^3$, and ~25 Å for an electron concentration of $10^{20}/cm^3$ [11]. The screening by a thin layer of electrons, however, is known to be less effective, and the screened Coulomb potential is proportional to $\sim 1/r^3$ in a 2-dimensional limit in contrast to $\sim(1/r)\cdot e^{-r/L}$ in a 3-dimensional case [12]. The characteristic screening length in the limit of degenerate 2-dimensional electron gas in GaAs is calculated to be ~45 Å, independent of the electron density [13,14]. The experimentally observed decrease of the extension of the protrusions, from ~50 Å at -1.5 V in weak accumulation to a minimum of about half that value at -3.0 V in strong accumulation, is thus in good agreement with what one would expect from the effect of screening by conduction electrons. For positive sample voltages, no such screening is expected since the surface is depleted of electrons, which is consistent with the experimental observation that the decrease of the extension of the protrusions is less significant with increasing positive sample voltages.

In conclusion, for the first time we have studied by scanning tunneling microscopy both the localized electronic features associated with the dangling-bond states of Si donors (Si_{Ga}) situated on GaAs(110) surface, and the delocalized electronic features associated with the Coulomb potential of the Si_{Ga} in bulk GaAs located below the (110) cleavage surface.

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FIGURE CAPTIONS

Fig. 1 STM topographic images of a Si_{Ga} on GaAs (110) cleavage surface. (a) Filled state STM image acquired at -2.5 V sample bias. (b) Empty state STM image acquired at +2.5 V sample bias. The locations of the Si_{Ga} is marked by the arrows in the images.

Fig. 2 STM images of the delocalized protrusions arising from subsurface Si_{Ga} taken with a tunneling current of 0.5 nA and at sample voltages of (a) -3.0 V; (b) -1.5 V. The topographic profile across the features along the line of the arrows in (a) and (b) is shown in (c). With increasing negative sample voltages, the apparent height and the spatial extension of the protrusions decreases.

Fig. 3 Schematic illustrations of the energy band diagrams and the electron tunneling processes. (a) at a positive sample voltage; (b) at a negative sample voltage. The dash lines in the figure illustrate the band perturbed by the subsurface Si_{Ga}.

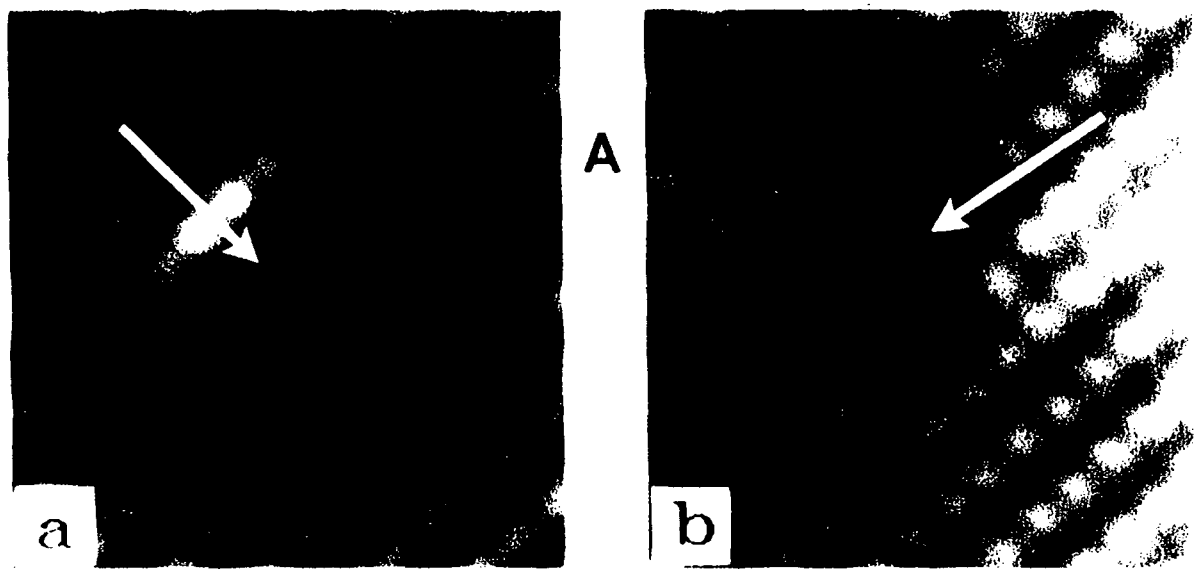


Fig. 1

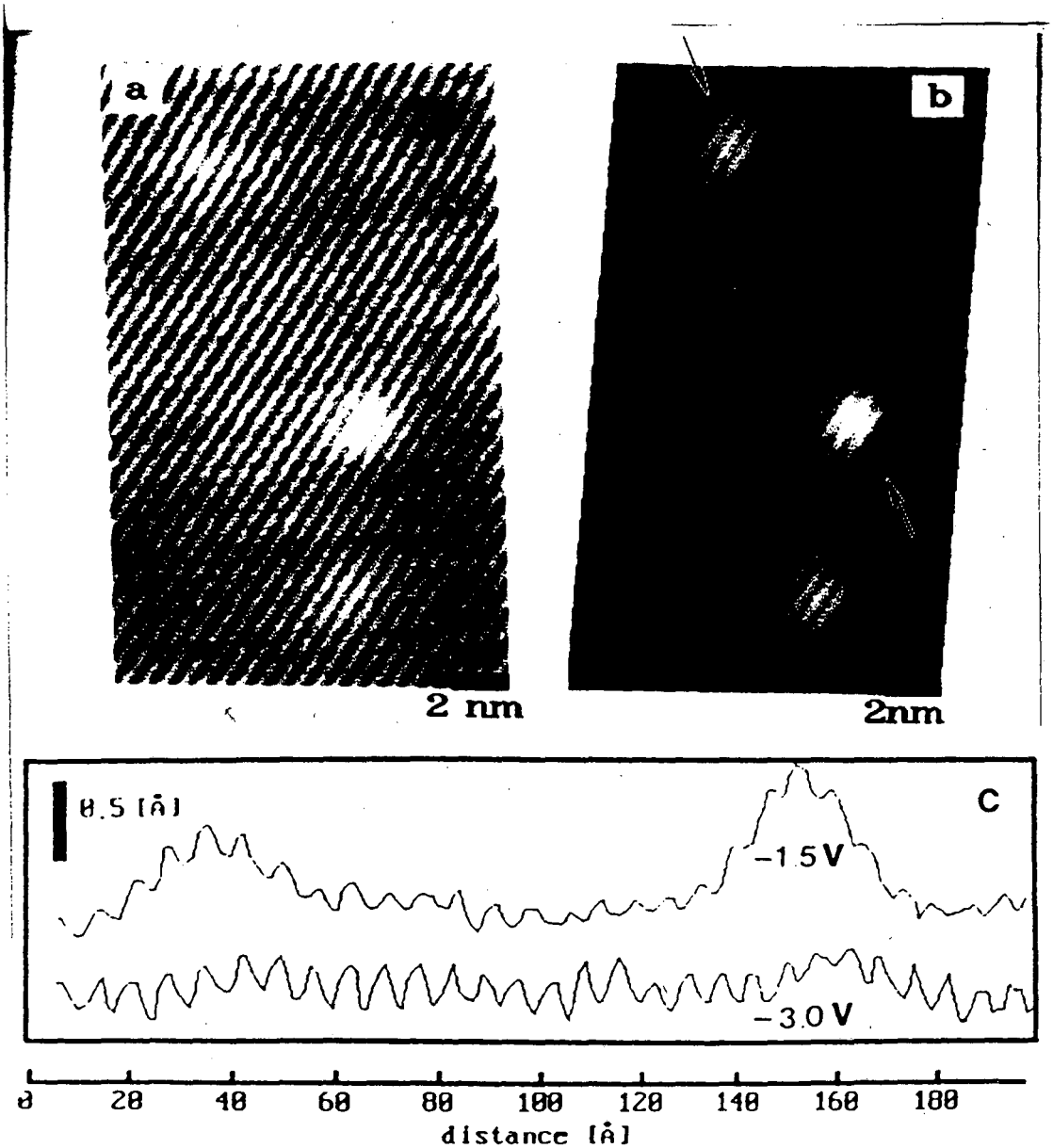
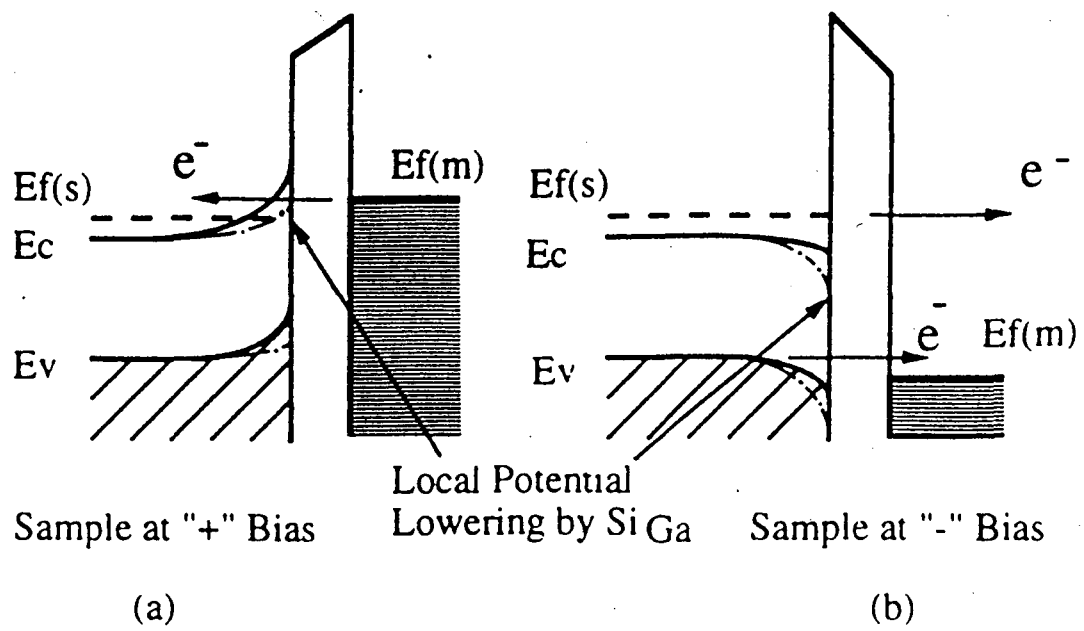

a
2 nm
b
2nm
0.5 [Å]
c
-1.5V
-3.0V
0
20
40
60
80
100
120
140
160
180
distance [Å]

Fig. 2


Ef(s)
e⁻
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Ec
Ev
Local Potential
Lowering by Si Ga
Sample at "+" Bias
(a)
Ef(s)
e⁻
Ec
e⁻
Ef(m)
Ev
Sample at "-" Bias
(b)

Fig. 3

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